# Possible fractal structure of exact universal exchange-correlation potential

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**Abstract:** Heuristic arguments are presented to show that the basic quantity of density functional theory - exact universal exchange-correlation potential should have fractal structure.

The fundamental equation describing electronic structure of matter is N-electron Schrödinger's equation

$$\left[\hat{T} + \hat{V} + \hat{U}\right] \Psi(\mathbf{r}_1, \mathbf{r}_2 \ldots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2 \ldots, \mathbf{r}_N), \tag{1}$$

where the kinetic energy operator

$$\hat{T} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2, \tag{2}$$

electron-nuclei interaction potential

$$\hat{V} = \sum_i v(\mathbf{r}_i) = -\sum_{ik} \frac{Z_k e^2}{|\mathbf{r}_i - \mathbf{R}_k|}, \tag{3}$$

the sum on $k$ run over all nuclei in the system, each with charge $Z_k e$ and position $\mathbf{R}_k$. And for a Coulomb system we have electron-electron interaction potential

$$\hat{U} = \sum_{i<j} U(\mathbf{r}_i, \mathbf{r}_j) = \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{4}$$

The usual quantum-mechanical approach to Schrödinger's equation (SE) can be summarized by the following sequence

$$v(\mathbf{r}) \overset{SE}{\Longrightarrow} \Psi(\mathbf{r}_1, \mathbf{r}_2 \ldots, \mathbf{r}_N) \overset{\langle\Psi|\ldots|\Psi\rangle}{\Longrightarrow} \text{observables}, \tag{5}$$

i.e., one specifies the system by choosing $v(\mathbf{r})$, put it into Schrödinger's equation, solves that equation for the wave function $\Psi$, and then calculates expectation values of observables with this wave function. Among the observables that are calculated in this way is also density

$$n(\mathbf{r}) = N \int d^3r_2 \int d^3r_3 \ldots \int d^3r_N \Psi^*(\mathbf{r}, \mathbf{r}_2 \ldots, \mathbf{r}_N)\Psi(\mathbf{r}, \mathbf{r}_2 \ldots, \mathbf{r}_N). \tag{6}$$

Many sophisticated methods for solving Schrödinger's equation have been developed, for example, diagrammatic perturbation theory [1], coupled cluster method [2], or Brillouin-Wigner coupled cluster method [3].

Nevertheless there is an attractive alternative to these methods, the density-functional approach (DFT) [4–7].

At the heart of DFT is the Hohenberg-Kohn theorem [9]. This theorem states that for ground states Eq. (6) can be inverted: given a *ground-state* density $n_0(\mathbf{r})$ it is possible, in principle, to calculate the corresponding *ground-state* wave function $\Psi_0(\mathbf{r}_1, \mathbf{r}_2 \ldots, \mathbf{r}_N)$. This means that $\Psi_0$ is a functional of $n_0$.

Recalling that the kinetic and interaction energies of a nonrelativistic Coulomb system are described by universal operators, we can N-electron energy functional $E_v$ write as

$$E_v[n] = T[n] + U[n] + V[n], \tag{7}$$

where $T[n]$ and $U[n]$ are *universal functionals*. On the other hand,

$$V[n] = \int d^3r \, n(\mathbf{r})v(\mathbf{r}) \tag{8}$$

is obviously nonuniversal (it depends on $v(\mathbf{r})$, i.e., on the system under study), but simple: once the system is specified, i.e., $v(\mathbf{r})$ is known, the functional $V[n]$ is known explicitly. All one has to do is to minimize $E_v[n]$ with respect to $n(\mathbf{r})$. The minimizing function $n_0(\mathbf{r})$ is the system's ground state charge density and the value $E_{v,0} = E_v[n_0]$ is the ground state energy. The problem is that the minimization of $E_v[n]$ is that the exact functional is not known and one needs to used approximations for $T[n]$ and $U[n]$.

In the Kohn-Sham approach the kinetic energy $T[n]$, is expressed in terms of the single-particle orbitals $\phi_i(\mathbf{r})$ of a noninteracting system with density $n$, as

$$T_s[n] = -\frac{\hbar^2}{2m} \sum_i^N \int d^3r \, \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}), \tag{9}$$

because for noninteracting particles the total kinetic energy is just the sum of the individual kinetic energies. Since all $\phi_i(\mathbf{r})$ are functionals of $n$, this expression for $T_s$ is an explicit orbital functional but an implicit density functional, $T_s[n] = T_s[\{\phi_i[n]\}]$.

We now rewrite the exact energy functional as

$$E[n] = T_s[n] + U[n] + V[n] = T_s[\{\phi_i[n]\}] + U_H[n] + E_{xc}[n] + V[n], \tag{10}$$

where $E_{xc}[n]$, is called the *exchange-correlation* (xc) energy functional, which incorporates correlations due to the Pauli exclusion principle, Coulomb repulsion, and also correlation contribution to the kinetic energy not included in Eq. (9).

Since $T_s$ is now written as an orbital functional one cannot directly minimize Eq. (10) with respect to $n$. Instead a scheme suggested by Kohn and Sham [10], is commonly employed for performing the minimization indirectly. This scheme starts by writing the minimization as

$$0 = \frac{\delta E}{\delta n} = \frac{\delta T_s}{\delta n} + \frac{\delta V}{\delta n} + \frac{\delta U_H}{\delta n} + \frac{\delta E_{xc}}{\delta n} = \frac{\delta T_s}{\delta n} + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}). \tag{11}$$

As a consequence of Eq. (8), $\delta V/\delta n = v(\mathbf{r})$, the 'external' potential the electrons move in. The term $\delta U_H/\delta n$ simply yields the Hartree potential $\int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$. The term $v_{xc}(\mathbf{r}) = \delta E_{xc}/\delta n$ is universal exchange-correlation potential.

Consider now a noninteracting system of particles moving in external potential $v_s(\mathbf{r})$. For this system the minimization condition is simply

$$0 = \frac{\delta E}{\delta n_s} = \frac{\delta T_s}{\delta n_s} + v_s(\mathbf{r}), \tag{12}$$

since there are no Hartree and $xc$ terms in the absence of interactions. Comparing this with the previous equation we find that both minimizations have the same solution $n_s(\mathbf{r}) \equiv n(\mathbf{r})$ if $v_s$ is chosen to be

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}). \tag{13}$$

Consequently, one can calculate the density of the interacting (many-body) system in potential $v(\mathbf{r})$ by solving the equations of a noninteracting (single-body) system in potential $v_s(\mathbf{r})$. In particular, the Schrödinger equation of this auxiliary system,

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{14}$$

yields orbitals that reproduce the density $n(\mathbf{r})$ of the original system,

$$n(\mathbf{r}) \equiv n_s(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2. \tag{15}$$

Eqs. (13) to (15) are the celebrated Kohn-Sham equations.

Since both $v_H$ and $v_{xc}$ depend on $n$, which depends on the $\phi_i$, which in turn depend on $v_s$, these equations should be solved till the self-consistency.

From converged solution $n_0$, the total ground-state energy can be calculated using

$$E_0 = \sum_i^N \epsilon_i - \frac{q^2}{2} \int d^3r \int d^3r' \frac{n_0(\mathbf{r})n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d^3r \, v_{xc}(\mathbf{r})n_0(\mathbf{r}) + E_{xc}[n_0]. \tag{16}$$

With the exact $v_{xc}(\mathbf{r})$ and $E_{xc}[n]$ all many-body effects are in principle included, which would be of tremendous importance for practical computational applications.

Let us consider the following one-dimensional Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{17}$$

If we have set of regularly ordered eigenvalues (e.g. $\epsilon_i = (i + \frac{1}{2})\hbar\omega$ for harmonic oscillator), the local potential $V(x)$ is given as a simple continuous function ($V(x) = \frac{1}{2}m\omega x^2$ in this case). But let us consider that the infinite set $\epsilon_i$ of eigenvalues is chosen randomly. The mystery of how a one-dimensional integrable system can produce any given eigenvalues is resolved by adopting [11] the concept of a fractal potential $V(x)$ which in the limit of infinite number of eigenvalues would have dimension higher than one. This principle can be illustrated on the example of nontrivial Riemann zeros, which were reproduced as an eigenvalues of Schrödinger equation with potential having dimension $d = 1.5$ [12], or on infinite the sequence of prime numbers, where $d = 1.8$ [13]. It has been even suggested that in the limit of infinity number of eigenvalues the fractal dimension should converge to $d = 2$ [14]. In the Kohn-Sham equation exchange-correlation potential $v_{xc}(\mathbf{r})$ should be universal, which mean that the exact values of ground-state density and energy should be obtained for uncountable infinity of $v(\mathbf{r})$ (all possible numbers of various nuclei at all possible positions in the space). Our suggestion is that in the analogy with the previous case this would be possible only when $v_{xc}(\mathbf{r})$ is a fractal function.

it is possible to invert Kohn-Sham equation and obtain exchange-correlation potential for a given N-electron system from highly correlated electronic densities computed with traditional methods of quantum chemistry. As has been recently found, commonly used approximate functionals have potentials that are not even remotely close to the potentials reconstructed from very precise *ab initio* calculations on the two-electron atoms [15]. Nevertheless it should be stressed that such an exchange-correlation potential is constructed for a given particular system (atom) and hence is not free from an implicit dependence on the given particular external potential and obtained expression for $v_{xc}$ is exact only for given atom and for all other atoms or molecules constitutes only an approximation to the ground-state density. In this sense such an approach is analogous to the local-density approximation which similarly replaces exact universal exchange-correlation potential by that of homogeneous electron gas with the same local density. It is natural that potentials obtained in such a way are different from approximate functionals because these are constructed in order to be universal (although approximate) for all atoms and molecules. The exact universal potential would be also different from such a particular atomic potentials.

For the reconstruction of genuine **universal** potential 10, 50 or maybe 100 atoms or molecules should be used simultaneously for iterative (till the Kohn-Sham equations would not reproduce exact densities for all atoms) reconstruction of $v_{xc}(\mathbf{r})$ as done in the analysis of Riemann zeros potential (the simplest system for such a study are spherically symmetric atoms, a one-dimensional systems where $v_{xc}$ is just a function of $r$, the radial distance from nuclei). Nevertheless this is not an easy task because very high numerical precision is needed (in the reconstruction of the potential producing Riemann zeros or primes several hundreds of eigenvalues were needed to reveal fractal structure of a potential). Another possibility is to represents universal $v_{xc}(\mathbf{r})$ as a trial fractal function with several parameters to be fitted.

Yet another possible way is to express the density-functional exchange and correlation potential in terms of the one-particle Green's function which in turn may be expressed in terms of the ground-state density Kohn-Sham orbitals [16]. In principle, this self-consistent loop yields the exact $v_{xc}(\mathbf{r})$.

The concept of a fractal potential has been already successfully exploited in the study of protein conformational dynamics [17], where has been found that the fractal dimension of of the total potential energy as a function of time is almost independent of temperature, and increases with time, more slowly the larger the protein. Perhaps the most striking observation of this study is the apparent universality of the fractal dimension, which depends only weakly on the type of molecular system.

It is interesting to note that both density functional theory [9,10] and Mandelbrot concept of fractals [18] emerged in the same time, about 40 years ago. We hope that our suggestion that fractals are also behind the density functional theory would be useful in searching for the exact universal exchange-correlation potential, the *Holy Grail* of many body physics.

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